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Effects of processing on the electrical and structural properties of spray deposited CdS:In thin films ☆

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ABSTRACT

Polycrystalline CdS:In thin films were prepared by the Spray pyrolysis technique (SP) at a substrate temperature $T_s = 490\,^{\circ}C$. The effects of annealing in nitrogen atmosphere at 400 °C and HCl-etching on the electrical and structural properties of the films were investigated. The electrical properties were studied through the analysis of the *I–V* curves, while the structural properties were studied through the analysis of the X-ray diffraction (XRD) patterns and the scanning electron microscope (SEM) images. An increase in the films' resistivity was occurred after annealing and/or HCl-etching, which was accompanied by changes in the XRD patterns and SEM images. These changes were related to a phase change from the mixed (cubic and hexagonal) phase to the hexagonal phase which was expected to occur during the aforementioned processes. The X-ray diffraction (XRD) patterns and the scanning electron microscope images confirm this expectation.

1. Introduction

Thin films of CdS have been extensively studied due to the variety of applications in optoelectronic devices. In particular heterojunction solar cells with a narrow bandgap base and a wide bandgap window such as CdS/CdTe and CdS/CuInSe solar cells [1].

There are several methods for depositing CdS thin films, such as; vacuum evaporation (VE) [2–4], chemical bath deposition (CBD) [1,5,6], spray pyrolysis (SP) [7–11], etc. However, the SP technique is a very low cost and simple technique that enables intentional doping and getting large area and uniform thin films [8]. Beside this it was found that in spray-deposited films a nanolayer originates from the interface between the polycrystalline film and the glass substrate [12]. As a result a gradient of trapping levels originates in the optical band gap which affects the optical and electrical properties of the films. This intermediate layer can play an important role in the performance of solar cell devices and electroluminescent displays [12]. Annealing enhances the formation of this nanolayer due to thermal stress which is due to the difference in expansion coefficients of the film and the substrate.

In this work polycrystalline CdS:In thin films were produced by the SP technique, and the effects of annealing in nitrogen atmosphere at 400 °C and HCl-etching on the electrical and structural properties of the films were investigated. The resistivity of the films was determined from the *I–V* plots which are linear. The structural properties were investigated through the X-ray diffraction (XRD) patterns and scanning electron microscope (SEM) images. A phase transition from the mixed (cubic and hexagonal) to the hexagonal phase was expected to occur after annealing at 400 °C and/or HCl etching. The XRD patterns and the SEM images confirm this expectation.

2. Experimental part

The precursor solution of CdS thin films was prepared by dissolving 2.06×10^{-2} mol of extra pure $CdCl_2 \cdot H_2O$ (MERECK Art.2011) and 2.24×10^{-2} mol of thiourea $(NH_2)_2CS$ (>97% S) in

☆ *Prime novelty statement*: The authors reported the phase transition of CdS from the mixed cubic and hexagonal phase to the hexagonal phase after HCl-etching and annealing in nitrogen for the first time.

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350 ml of distilled water. Indium chloride $InCl_3$ (MERECK Art.12471) was used as a doping compound. The ratio of the concentration of indium ions to that of cadmium ions in the solution which is not necessarily the same as their ratio in the films was considered as an estimation of the doping ratio. Two doping ratios were considered: 1.0×10^{-4} and 1.5×10^{-2}. The solution was sprayed intermittently by using the spraying system described in Ref. [8] on glass substrates that were ultrasonically cleaned with methanol at a substrate temperature $T_s = 490\,^{\circ}C$.

The solution that was used for etching CdS:In thin films was HCl (about 36% HCl) in distilled water (1:100 by volume). The films were dipped in this solution for about 20 s, rinsed in distilled water and dried by an air drier. Annealing was established at 400 °C in nitrogen atmosphere by the annealing system described in Ref. [8].

The films' thickness was in the range 0.2–1.0 μm. It was estimated by using Lambert law for absorption in a semiconductor. That is by making use of the relative transmittance through each film at a certain wavelength which was measured by a double beam Shimadzu UV 1601 (PC) spectrophotometer.

Aluminum and indium were chosen to make the contacts, where two strips of the contact material were deposited on the surface of the film by vacuum evaporation. The contacts have a thickness of more than 0.4 μm, a length of 1 cm, a width of 1 mm, and a separation of 2–3 mm. The *I–V* measurements were taken by using a Keithley 2400 Source Meter, which was interfaced by an IBM personal computer. The samples were placed in a brass cell that had a cover to enable measurements in the dark.

XRD measurements were made with a Philips PW1840 Compact X-ray diffractometer system with Cu K_α ($\lambda = 1.5405$ Å). The diffraction angle 2θ was varied from 2° to 60° in steps of 0.04°, and the peaks in the obtained diffraction patterns were identified.

The SEM images of the CdS:In thin films were taken by a LEITZ-AMR 1000A scanning electron microscope. The film was covered with a sputtered gold layer (~20 nm) before taking the measurements. The purpose of this layer was to prevent sample charging effects.

3. Results and discussion

3.1. The electrical properties

The *I–V* characteristics were recorded in the dark at room temperature and displayed in Fig. 1. The plots are linear and the slopes were used to find the resistivity of the films. For the two doping ratios tried in this work, the *I–V* plots are shown in Fig. 1a. The resistivity of the films had decreased from $\rho = 4.63 \times 10^7\,\Omega\,cm$ for the doping ratio 1.0×10^{-4}, to $\rho = 900\,\Omega\,cm$ for the doping ratio 1.5×10^{-2}, or a decrease by a factor of more than 5.1×10^4. So indium doping had significantly decreased the resistivity of the films. The effect of doping on the properties of CdS films is not the subject of this work, but it was investigated by many authors [3,7,8].

The effect of annealing in nitrogen atmosphere at 400 °C on the electrical properties of CdS:In thin films was also investigated by recording the *I–V* plots of the films at room temperature in the dark which are shown in Fig. 1b. Aluminum contacts were used here rather than indium contacts because indium diffuses in the film during the annealing process and changes the doping ratio

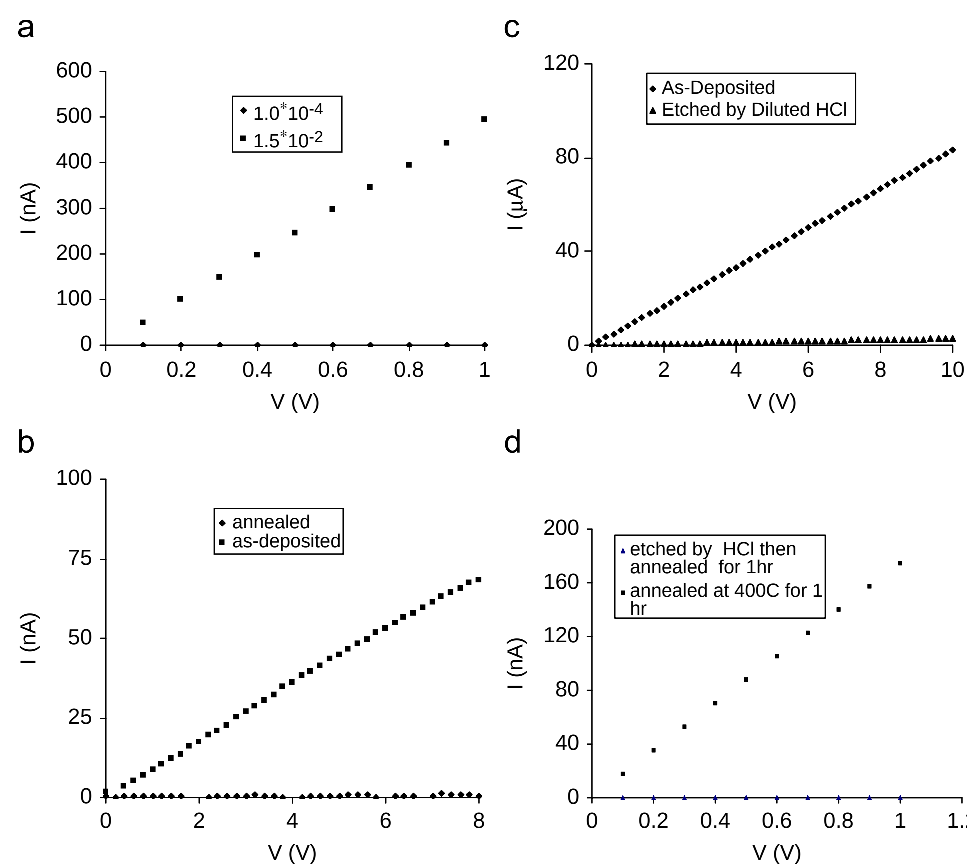

Fig. 1. The *I–V* plots for CdS:In thin films. (a) Two films with two different doping ratios. (b) A film of doping ratio of 1.5×10^{-2} with Al contacts before and after annealing in nitrogen atmosphere at $T = 400\,^{\circ}C$. (c) A film of doping ratio of 1.5×10^{-2} with In contacts before and after HCl-etching. (d) Two films, one of them was HCl-etched before annealing and the other was not etched.